# THE RATE CONSTANTS OF THE REACTIONS OF NITROSYL CHLORIDE WITH CHLORINE ATOMS AND COCI RADICALS

BY W. G. BURNS AND F. S. DAINTON Department of Inorganic and Physical Chemistry, The University, Leeds 2

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The kinetics of the photochemical formation of phosgene using light of wavelength 3660 Å and in the presence of minute amounts of nitrosyl chloride have been investigated at 25°, 40° and 55° C. The observed rate law is

 $\frac{\mathrm{d}[\mathrm{COCl}_2]}{\mathrm{d}t} = \frac{I_{\mathrm{abs}}[\mathrm{CO}][\mathrm{Cl}_2]}{[\mathrm{NOCl}]\{B[\mathrm{CO}] + C\}},$ 

which is in accord with the reaction scheme proposed by Dainton,<sup>1</sup> viz.,  $Cl_2 + h\nu \rightarrow 2Cl$ ,  $Cl + CO \rightleftharpoons COCl$ ,  $COCl + Cl_2 \rightarrow COCl_2 + Cl$ ,  $Cl + NOCl \xrightarrow{k_6} NO + Cl_2$ ,  $COCl + NOCl \xrightarrow{k_7} Cl_2 + CO + NO$  (or  $COCl_2 + NO$ ). Combining the measurements with the results of the previous paper, the experimental values  $k_6 = 10^{10.06} \exp(-1.06 \text{ kcal/}RT)$ and  $k_7 = 10^{10.68} \exp(-1.14 \text{ kcal/}RT)$  l. mole<sup>-1</sup> sec<sup>-1</sup> were deduced.

The potential energy diagram for reaction (6) was calculated on the assumptions (a) that the NO unit can be treated as an atom, (b) that 20 % of the binding is coulombic, and (c) that the problem may be treated as a three S electron problem. A relation has been obtained which shows that the activation energy depends critically on the arbitrarily

chosen fraction of the binding which is coulombic. Assuming also a transmission coefficient of unity, the theoretical value of  $k_6^{25^\circ}$  becomes  $10^{12 \cdot 52} \exp(-2.02 \text{ kcal/}RT)$ .

The velocity constant of the reaction  $Cl + ICl \rightarrow I + Cl_2$  has been calculated by similar methods and the value obtained is  $x \cdot 10^{10.2} \exp(-2.35 \text{ kcal/RT})$ , where x is the unknown transmission coefficient. Preliminary experiments are reported which indicate that iodine monochloride retards the photochemical formation of phosgene but is less efficient than nitrosyl chloride.

Nitrosyl chloride is a very efficient retarding agent for the photochemical formation of phosgene from carbon monoxide and chlorine. Some of the principal features of the kinetics of this reaction have been reported by Dainton <sup>1</sup> who measured the dependence of the inhibited rate on the partial pressures of carbon monoxide, chlorine and nitrosyl chloride at constant temperature and constant incident light intensity. His results may be summarized in the expression

$$\frac{\mathrm{d}[\mathrm{COCl}_2]}{\mathrm{d}t} = \frac{[\mathrm{CO}][\mathrm{Cl}_2]^n}{[\mathrm{NOCl}]\{B[\mathrm{CO}] + C\}},\tag{1}$$

where B and C are constants, and n = 2 at low partial pressures of chlorine decreasing to lower values at higher partial pressures. Assuming that the term  $[Cl_2]^n$  really represented  $[Cl_2]I_{abs}^{1.0}$  this author showed that the experimental law is in accord with the Bodenstein mechanism for the uninhibited reaction provided two simultaneous chain ending reactions, each involving nitrosyl chloride ((6) and (7) below), are substituted for the mutual termination reaction (5)

(5) 
$$\operatorname{COCl} + \operatorname{Cl} \rightarrow \operatorname{CO} + \operatorname{Cl}_2.$$

The complete reaction scheme is then

(1) 
$$Cl_2 + h\nu \rightarrow 2Cl$$

(2)  
(3) 
$$Cl + CO \rightarrow COCl$$
  
 $COCl \rightarrow CO + Cl$   
 $K_{cocl} = \frac{[CO][Cl]}{[COCl]}$ 

$$(4) \qquad \qquad \operatorname{COCl} + \operatorname{Cl}_2 \to \operatorname{COCl}_2 + \operatorname{Cl}_2$$

(6) 
$$Cl + NOCl \rightarrow NO + Cl_2$$

(7) 
$$\operatorname{COCl} + \operatorname{NOCl} \rightarrow \operatorname{NO} + \operatorname{CO} + \operatorname{Cl}_2$$

leading to

$$\frac{d[\text{COCl}_2]}{dt} = \frac{2k_1k_2k_4[\text{CO}][\text{Cl}_2]I_{\text{abs}}}{[\text{NOCl}]\{k_7k_2[\text{CO}] + k_6(k_3 + k_4[\text{Cl}_2] + k_7[\text{NOCl}])\}}$$
(2)

and provided the equilibrium  $CO + Cl \rightleftharpoons COCl$  is maintained, i.e.

$$k_3 \gg k_4[Cl_2] + k_7[NOCl],$$

and the chains do not become too short, this becomes

$$\frac{d[COCl_2]}{dt} = \frac{2k_1k_4[CO][Cl_2]I_{abs}}{[NOCl]\{k_7[CO] + k_6K_{cocl}\}}$$
(3)

Since  $K_{\text{cocl}}$  and  $k_4$  are known (see preceding paper <sup>2</sup>), the graph of [CO]/rate against [CO] should enable  $k_6$  and  $k_7$  to be determined.

The purpose of the experiments described in part I of the present paper was to verify the rate law of eqn. (3) and from these data and absolute measurement of  $I_{abs}$  to obtain values of  $k_6$  and  $k_7$  at different temperatures. Values of the frequency factors and energies of activation of the reactions (6) and (7) could then be calculated and compared with the values of these quantities calculated theoretically in a manner described in part II.

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#### Part I.—The determination of $k_6$ , $k_7$ , $E_6$ and $E_7$ experimentally

EXPERIMENTAL.—The apparatus, the methods of preparation of carbon monoxide and chlorine, and the methods of following the reaction were identical with those described in the preceding paper on the uninhibited reaction.<sup>2</sup> The nitrosyl chloride was made and analyzed as described.<sup>3</sup>

RESULTS.—As in the uninhibited reaction there is an initial pressure rise due to the exothermicity of the reaction (Draper effect) after which the rate is constant for a considerable pressure fall and then decelerates. When pure nitrosyl chloride was used no induction period was observed, nor did the reaction show any sign of acceleration.

The dependence of the rate on  $I_{abs}$ .—The incident light intensity was varied over a five-fold range by running the variable angle sector at constant high speed (2000 rev/min) but at different angles of opening. The results for 25° C and an



FIG. 1.—The dependence of the rate on  $I_{abs}$ .  $P_{CO} = P_{Cl_2} = 300 \text{ mm Hg}$ ;  $P_{NOCl} = 0.0028 \text{ mm Hg}$ ;  $T = 25^{\circ} \text{ C}$ ; 100 scale mm  $\equiv 10.5 \text{ mm Hg}$ .

equimolar mixture of reactants containing  $8.3 \times 10^{-4}$  mole per cent of nitrosyl chloride are shown in fig. 1 from which the rate may be seen to be quite accurately proportional to  $I_{abs}^{1.0}$ . Further evidence for this conclusion was obtained by making runs with a sector of constant angle over a wide range of speeds (59 to 3000 rev/min) when it was found that the *maximum* percentage deviation from the mean rate was only 1.3 %.

Dependence of the rate on nitrosyl chloride concentration.—Fig. 2 illustrates runs made at constant [CO], [Cl<sub>2</sub>] and temperature and corrected to constant intensity of light absorbed. The graph of rate against  $P_{\text{Nocl}}^{-1}$  is nearly straight but does not pass through the origin. This was thought to be due to the chain ending reaction (7) producing phosgene molecules, i.e.

$$COCl + NOCl \rightarrow COCl_2 + NO$$
,

in which case the rate expression (3) should be increased by an amount

$$\Delta\left(\frac{\mathrm{d}[\mathrm{COCl}_2]}{\mathrm{d}t}\right) = 2I_{\mathrm{abs}}\{1 + K_{\mathrm{cocl}} k_6/k_7[\mathrm{CO}]\}^{-1} \tag{4}$$

However, this amounts to only one-tenth of the observed intercept. Other contributory factors might be (a) the fact that at very low values of [NOCI] the chain ending step (5) must play some part, and (b) that at very large values of



FIG. 2.—The dependence of the rate on nitrosyl chloride concentration,  $P_{co} = P_{cl_2}$ = 300 mm Hg;  $T = 25^{\circ}$  C; 100 scale mm = 10.5 mm Hg.



FIG. 3.—Dependence of the rate on chlorine concentration.  $P_{\rm CO} = 300$  mm Hg;  $P_{\rm NOCI} = 0.0028$  mm Hg;  $T = 25^{\circ}$  C; 100 scale mm  $\equiv 10.5$  mm Hg.

[NOCI] the equilibrium  $CO + Cl \rightleftharpoons COCl$  will no longer be maintained. The intercept is very slight, however, and fig. 2 will be taken as satisfactory evidence that the rate is inversely proportional to the partial pressure of nitrosyl chloride.

Dependence of the rate on chlorine concentration.—The fraction of the light absorbed varies with the partial pressure of chlorine and in order to compare rates under comparable conditions of absorbed light, due allowance was made for this effect and also for repeated internal reflections.<sup>4</sup> Fig. 3 shows the observed rate divided by a factor f, which corrects for these two effects, plotted against



chlorine pressure. This graph is a straight line up to 150 mm only, after which deviations from linearity fall outside the experimental error. The cause of these deviations is probably the growth of the term  $k_4[Cl_2]$  as compared with  $k_3$  in the denominator of eqn. (2).

Dependence of the rate on carbon monoxide concentration and on temperature. Fig. 4 shows clearly that [CO]/rate is proportional to [CO] and thereby provides

proof of the occurrence of the chain breaking reaction (7). The variation of the rate with carbon monoxide pressure was also measured at  $40^{\circ}$  and  $55^{\circ}$  C and the curious phenomenon was observed of the rate decreasing with rise of temperature at low pressures of carbon monoxide, and increasing at high pressures. This can be explained by referring to the rate expression, the limiting values of which are

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{COCl}_2] = \frac{2I_{\mathrm{abs}}[\mathrm{Cl}_2][\mathrm{CO}]}{[\mathrm{NOCl}]} \cdot \frac{k_1 k_4}{k_6 K_{\mathrm{cocl}}} \text{ at low pressures,}$$
(5)

and

$$\frac{d}{dt}[COCl_2] = \frac{2I_{abs}k_1k_4[Cl_2]}{[NOCl]k_7} \text{ at high pressures of CO.}$$
(6)

At low pressures the rate will decrease as the temperature rises since  $K_{\text{cocl}} k_6$  increases more rapidly than  $k_4$ , and at high pressures the rate will increase since reaction (4) has a higher activation energy than reaction (7).

#### DISCUSSION

The results obtained fit in very well with the rate law obtained by substituting for reaction (5) in the scheme for the uninhibited reaction the chain ending steps

(6) 
$$Cl + ClNO \rightarrow Cl_2 + NO$$

$$\operatorname{COCl} + \operatorname{ClNO} \rightarrow \operatorname{CO} + \operatorname{Cl}_2 + \operatorname{NO}$$

(7) 
$$\searrow$$
 COCl<sub>2</sub> + NO

We leave the question of the products of reaction (7) for later discussion. The NOCl is removed in reactions (6) and (7) to give nitric oxide, but there is reason to believe that this is rapidly restored by the reaction

$$(8) 2NO + Cl_2 \rightarrow 2 NOCl$$

since the reaction rate falls off smoothly with increasing time as the reactants are used up. The NO formed would not be expected to inhibit at the same rate as NOCl, and if reactions (6) and (7) were operating without a back reaction, they would remove the usual amounts of NOCl used, in the first two minutes, and produce an abrupt change in the pressure against time graph. The fact that the pressure against time graph is a smooth one, right from the instant of illumination, leads us to the view that reaction (8) is sufficiently fast to maintain the original concentration of NOCl, and by making measurements of the initial slope of the pressure against time graph, we ensure that the measurements are made at the initial concentrations of the reactants.

From the graphs of [CO]/rate against [CO] at various temperatures, making all due corrections and using the values of  $k_1$  and  $k_4$  given in the previous paper, we find that

$$k_6 = 10^{10.06} \exp\left(-1.06 \, \text{kcal}/RT\right) \tag{7}$$

and

$$k_7 = 10^{10.68} \exp\left(-1.14 \text{ kcal}/RT\right)$$
 (8)

the error in the frequency factors being about 10 % and in the *E* values about 30 %.

## Part II.—Theoretical evaluation of the velocity constant $k_6$

(a) ACTIVATION ENERGY.—Using the semi-empirical method,<sup>5</sup> the potential energy contours of reaction (6)

$$ON-Cl + Cl \rightarrow NO + Cl-Cl$$

have been determined and are shown on a rectangular diagram in fig. 5. For the purpose of this calculation it was necessary to assume that the unit NO behaves as an atom. The justification of this assumption is that the NO unit has roughly the same interatomic distance and vibration frequency in nitrosyl chloride  $^{6}$  as

in nitric oxide.<sup>7</sup> The bond dissociation energy  $D_{oN-Cl}$  is known and we have used Beeson and Yost's assignments <sup>6b</sup> of vibration frequencies deduced from Bailey and Cassie's spectroscopic data.<sup>6a</sup> These assignments have recently been confirmed by Bernstein and Burns <sup>6c</sup> who give 1799, 592 and 332 cm<sup>-1</sup> for the N $\leftrightarrow$ O, N $\leftrightarrow$ Cl and breathing frequencies respectively.

To use the London equation in calculations of this kind it is necessary to know what fraction ( $\sigma$ ) of the total binding energy is coulombic. The value chosen was 20 % because, although  $\sigma$  should exceed 50 % for p electrons, many problems of



FIG. 5.—Potential energy diagram for the reaction NOCl + Cl  $\rightarrow$  NO + Cl<sub>2</sub>.  $r_1 =$  Cl . . . Cl distance,  $r_2 =$  N . . . Cl distance, contours at 5 kcal intervals. X denotes points of maximum energy on the reaction path.

this type have been worked out with reasonable success using 20 %. The contour map computed on this basis (fig. 5) has the following features :

- (i) the energy of activation is small ( $\sim 1$  kcal);
- (ii) the complex NOCl<sub>2</sub> has a low stability, with a heat of formation of 20.8 kcal from NOCl + Cl and of 2.6 kcal from NO + Cl<sub>2</sub>;
- (iii) the two maxima of the reaction path in the direction of the equation are at the points marked X with co-ordinates  $(r_1 = 3.15\text{\AA}, r_2 = 1.95\text{\AA})$  and  $(r_1 = 2.00\text{\AA}, r_2 = 2.50\text{\AA})$  and have energies -37.7 and -55.4 kcal respectively, so that the easiest way out of the potential basin is in the direction forming the products.

The accurate calculation of the semi-empirical activation energy is simplified in this, as in many similar reactions, by the fact that  $r_1 + r_2$  is very large and the bond to be broken has not been extended. This has two consequences. Firstly  $C + \gamma$  can be neglected and we can write for the total energy E of the system:

$$E = \sigma(E_{\rm A} + E_{\rm B}) - (1 - \sigma)(E_{\rm A}^2 + E_{\rm B}^2 - E_{\rm A}E_{\rm B})^{\frac{1}{2}}.$$
 (9)

Secondly, since  $r_2$  is constant in the region of the activated complex,  $E_B = D_B$ (dissociation energy of the bond to be broken) in this region. The value of  $E_A$ at the complex may then be obtained by writing dE/d (reaction path) =  $dE/dr_1 = 0$ , or more conventionally putting  $dE/dE_A = 0$  and  $E_B = D_B$  in eqn. (9). The activation energy is thus only dependent on  $\sigma$  and the energy ( $-E_B$ ) of the bond broken. In fig. 6 we have plotted the ratio of the activation energy to the energy of the bond which is broken as a function of  $\sigma$ , from which it is seen that  $E_6$  varies very markedly with  $\sigma$ . Taking  $\sigma = 20 \%$ , the activation energy, corrected for the residual energies of the complex and reactants is 1.13 kcal and the dimensions of the complex are  $r_1 = 3.12$  Å and  $r_2 = 1.95$  Å.

(b) THE VELOCITY CONSTANT.—The evaluation of the velocity constant involves a knowledge, not only of the dimensions of the complex but also of its fundamental vibration frequencies. The calculation of these latter quantities was carried out by the usual method,<sup>5</sup> being made simpler by the fact that  $C + \gamma$  is quite negligible in this case, so that the force constants  $b_{12} = b_{21} = 0$ .

The values obtained were

$$v_{s}(i) = 604.6 \text{ cm}^{-1},$$
  
 $v_{l} = 67.1 \text{ cm}^{-1},$   
 $v_{\phi} = 2.87 \text{ cm}^{-1}.$ 

It is to be noted that for the purpose of calculating these frequencies the unit NO was regarded as an atom of mass 30 and the bending frequency  $v_{\phi}$  is therefore



FIG. 6.-Variation of activation energy with percentage coulomb energy.

doubly degenerate. Also required for the calculation of the velocity constant are the rotational partition functions of the complex and nitrosyl chloride, and for this purpose it was considered that the fiction of the linearity of these two molecules could not be maintained. The moments of inertia *I* of nitrosyl chloride are 9.05, 147.7 and 156.7 ( $\times$  10<sup>-40</sup> g cm<sup>2</sup>)<sup>60</sup> and, assuming that the length of the NO bond and the angle it makes with the N—Cl bond are unaltered in the complex, the three moments of inertia of this molecule are 20.9, 794.7 and 815.6 ( $\times$  10<sup>-40</sup> g cm<sup>2</sup>).

The velocity constant of reaction (6) is thus given by

$$k_{6} = \kappa \frac{g_{+}}{g_{cl}g_{NOCl}} \left(\frac{m_{+}}{m_{cl}m_{NOCl}}\right)^{3/2} \frac{\hbar^{2}}{(2\pi)^{3/2}(kT)^{\frac{1}{2}}} \frac{(I_{1}I_{2}I_{3})^{\frac{1}{2}}}{(I_{1}I_{2}I_{3})^{\frac{1}{2}}_{NOCl}} \frac{\sigma_{NOCl}}{\sigma_{+}} \frac{\left\{1 - \exp\left(-\frac{\hbar\nu_{N-Cl}}{kT}\right)\right\}}{\Pi\left\{1 - \exp\left(-\frac{\hbar\nu_{+}}{kT}\right)\right\}} \times \exp\left(-\frac{E_{0}}{RT}\right) \operatorname{cm}^{3} \operatorname{mole}^{-1} \operatorname{sec}^{-1}, \quad (10)$$

where g denotes electronic statistical weight, m mass,  $\sigma$  symmetry number,  $\nu$  vibration frequency,  $\kappa$  transmission coefficient, the subscript  $\pm$  refers to the complex, and **h**, **k** and **T** have their usual significance. The values of the relevant frequencies are  $\nu_{N-Cl} = 592 \text{ cm}^{-1}$ ,  $6^{\sigma}$  and  $\nu_{\phi}$  and  $\nu_{l}$  as given above. The value of the constant at 25° C is then given by

$$(k_6^{25^\circ})_{calc} = \kappa \times 7.32 \times 10^{11} \times \exp(-1.13 \text{ kcal}/RT)$$
 l. molecule<sup>-1</sup> sec<sup>-1</sup>. (11)

The resemblance of the contour map for this reaction to that evaluated by Steiner and Rideal <sup>8</sup> for the reaction,  $HCl + D \rightarrow H + ClD$ , raises the question as to whether the transmission coefficients are also similar, i.e. of the order of  $10^{-3}$ . However, this is unlikely since the origin of the low transmission coefficient in Steiner and Rideal's case was primarily that the angle (87° 48') at which the axes were required to be set for the energy changes undergone by a mass point sliding on the surface to represent the energy changes during their reaction, was so nearly 90°. In our case, however, the requisite angle between the axes is 61° 25'. There is therefore a strong interaction between the Cl—NO and Cl—Cl vibrations and reflection is unlikely. A large error will not be occasioned by taking the transmission coefficient to be unity, and writing

$$(k_6^{25^\circ})_{\text{calc}} = 7 \times 10^{11} \exp(-1.13 \text{ kcal}/RT) \text{ l. mole}^{-1} \sec^{-1}.$$
 (12)

When the assumptions involved in the calculations are considered, the disparity between the experimental and theoretical values of  $k_6^{25^\circ}$  does not appear excessive. However, it must be remembered that the experimental activation energy (1.06 kcal) is derived from the temperature coefficient, i.e.  $E_{6obs} = RT^2 d \ln (k_{6obs})/dT$  and should not be compared with the theoretical value for the activation energy at the absolute zero (1.13 kcal), but with the value of  $RT^2 d \ln (k_{6als}^{25^\circ})$  /dT which we shall call the Arrhenius activation energy at 25° \* and which is given by

$$RT^{2} \frac{\mathrm{d} \ln (k_{6}^{25})_{\mathrm{calc}}}{\mathrm{d}T} = \left\{ 1.13 - \frac{0.298R}{2} + Nh\left(\sum_{k=1}^{3} \nu_{\pm}\left(\exp\left(\frac{h\nu_{\pm}}{kT}\right) - 1\right)^{-1} - \nu_{\mathrm{N-cl}}\left(\exp\left(\frac{h\nu_{\mathrm{N-cl}}}{298k}\right) - 1\right)^{-1} \right\} \, \mathrm{kcal} \quad (13)$$

Due to the low value of the frequency of the doubly degenerate bending vibration, the corrections are large and the theoretical value of the Arrhenius activation energy at 25° C is 2.02 kcal, which is considerably larger than the experimental value of 1.06 kcal. Furthermore, if this value is placed in the Arrhenius type velocity constant expression  $(k_{calc}^{25^{\circ}} = A_{calc}^{25^{\circ}} \exp(-2.02 \text{ kcal}/RT))$  the value of  $A_{calc}^{25^{\circ}}$  becomes  $3.35 \times 10^{12}$  l. mole<sup>-1</sup> sec<sup>-1</sup> which is widely different from the observed frequency factor of  $1.15 \times 10^{10}$  l. mole<sup>-1</sup> sec<sup>-1</sup>. The discrepancy between theory and experiment, which involves both the frequency factor and the Arrhenius activation energy has been stated to be due to the low bending frequency in the complex which in turn is probably caused by the application to a three *p*-electron system a method only valid for *s* electrons. The calculation thus results in a more spread out and loosely bound structure than seems actually to occur.

CONCLUSIONS.—The use of the rotating sector technique in the study of uninhibited photochlorination reactions which proceed by a chain mechanism involving mutual termination enables the rate constants of both propagation steps and the termination reaction to be determined. An example of the application of this method was given in the preceding paper. When retarding agents are added which exert their actions merely by replacement of the mutual termination step by reaction of the Cl atom and/or the other chain carrier with the retarding agent, the rate constants of these new reactions can easily be deduced from the

\* We are indebted to the referee for this terminology.

kinetics of the retarded reaction combined with the values of the propagation constants "carried over" from the uninhibited reaction. When nitrosyl chloride is used as the retarding agent in the photochemical formation of phosgene it reacts with both the chain carriers, i.e. Cl and COCl. The former reaction has a velocity constant

 $k_6 = 10^{10.06} \exp(-1.06 \text{ kcal}/RT)$  l. mole<sup>-1</sup> sec<sup>-1</sup>.

Assuming (a) that the NO unit may be treated as an atom, (b) that 20 % of the total binding is coulombic, (c) that the transmission coefficient is unity, and (d) that the problem may be treated as a 3s electron problem, the semi-empirical method leads to a velocity constant of  $10^{12.52} \exp(-2.02 \text{ kcal/RT})$ . The drastic



FIG. 7.—Potential energy diagram for the reaction I Cl + Cl  $\rightarrow$  I + Cl<sub>2</sub>.  $r_1$ =Cl . . . Cl distance,  $r_2$  = I . . . Cl distance. Contours at 5 kcal intervals. X denotes points of maximum energy on the reaction path.

nature of assumptions (c) and (d) and the sensitivity of the calculated value of the energy of activation to the arbitrarily chosen coulombic fraction of the binding energy detracts enormously from any significance attached to any agreement of the calculated and experimental values of  $k_6$ . The most important feature of the experimental value is that the frequency factor is "normal", i.e. not far removed from the collision rate, as would be expected for a simple radical replacement reaction. With these considerations in mind the calculation of a theoretical value for the rate constant of the reaction of NOCl with COCl is not profitable and has not been undertaken. The experimental value of

$$10^{10.68} \exp(-1.14 \text{ kcal}/RT)$$

is also normal in respect of the frequency factor and does not afford a criterion as to whether  $COCl_2 + NO$  or  $CO + Cl_2 + NO$  are the more likely products.

THE REACTION ICl + Cl  $\rightarrow$  I + Cl<sub>2</sub>.—On general considerations we expected that this exothermic reaction would take place almost as readily as reaction (6)

and that the ICl concentration might be maintained when excess chlorine was present. Iodine monochloride should therefore be a powerful retarding agent of photochlorination reactions. Before testing this view experimentally the semi-empirical method was used to calculate the velocity constant in exactly the same way as for reaction (6). The potential energy surface is shown in fig. 7 and is similar to the one for reaction (6) except that the complex is more stable. The value of  $E_0$  is 1.46 kcal and corrections for residual energy differences are negligible. The complex I--Cl--Cl has an energy of formation of 12.9 kcal from ICl + Cl and of 5.4 kcal from I + Cl<sub>2</sub>. The configuration of the activated  $-3-00 \rightarrow \leftarrow 3-21 \rightarrow$ Cl Cl, and a transmission coefficient approaching unity complex is I is to be expected since the inclination of the axes in the energy contour map is so acute ( $51^{\circ}$  20'). Allowing for the temperature dependence of the frequency factor we obtain

 $k(ICI + CI \rightarrow I + Cl_2) = 10^{10.2} \exp(-2.35 \text{ kcal}/RT) \text{ l. mole}^{-1} \text{ sec}^{-1}$ . (14)

Some preliminary "experiments" were attempted in order to compare the reactivity of NOCl with that of ICl with Cl atoms. Iodine monochloride was purified by fractional crystallization in an evacuated vessel, then introduced into a reservoir with a vacuum Verschluss and sealed off. Because of its ready reactions with chlorine to form a canary yellow deposit of ICl3 and also with tap grease, a very dilute mixture (0.1 volume %) in carbon monoxide was made up just before use. The appropriate amount of this mixture was placed in the reaction vessel, then carbon monoxide and lastly chlorine were added; after which illumination was begun without any delay for mixing. The pressure against time graphs were of the same form as for nitrosyl chloride and at 25° C the plot of rate against  $P_{1c1}^{-1}$  for  $P_{co} = P_{cl_2} = 300$  mm gave a straight line passing through the origin. The magnitude of the retardation is slightly less for ICl than for NOCl, in keeping with the relative magnitude of the theoretical rate constants. Further work with this and other inhibitors on other photochlorination reactions is projected and will be reported in due course.

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<sup>&</sup>lt;sup>1</sup> Dainton, Trans. Faraday Soc., 1947, 43, 365.

<sup>&</sup>lt;sup>2</sup> Burns and Dainton, Trans. Faraday Soc., 1952, 48, 39.

<sup>&</sup>lt;sup>3</sup> Burns and Dainton, Trans. Faraday Soc., 1952, 48, 21.

<sup>&</sup>lt;sup>4</sup> Hunt and Hill, J. Chem. Physics, 1947, 15, 111.

<sup>&</sup>lt;sup>5</sup> Glasstone, Laidler and Eyring, The Theory of Rate Processes (New York, 1941).

<sup>&</sup>lt;sup>6</sup> (a) Bailey and Cassie, Proc. Roy. Soc. A, 1934, 145, 336; (b) Beeson and Yost J. Chem. Physics, 1939, 7, 44; (c) Bernstein and Burns, J. Chem. Physics, 1950, 18, 1669. <sup>7</sup> Gillette and Eyster, Physic. Rev., 1939, 56, 1113.

<sup>&</sup>lt;sup>8</sup> Steiner and Rideal, Proc. Roy. Soc. A, 1939, 173, 503.